



12 **EUROPEAN PATENT APPLICATION**

21 Application number: 93303542.0

51 Int. Cl.⁵: H05K 3/00, G03F 7/20

22 Date of filing: 07.05.93

30 Priority: 20.07.92 IL 102554
23.12.92 US 995687
07.01.93 US 1342

Waterbury, Connecticut 06702(US)

43 Date of publication of application:
25.08.93 Bulletin 93/34

72 Inventor: The designation of the inventor has not yet been filed

84 Designated Contracting States:
BE CH DE FR GB IT LI LU NL

74 Representative: Pendlebury, Anthony et al
PAGE, WHITE & FARRER 54 Doughty Street
London WC1N 2LS (GB)

71 Applicant: MACDERMID, INCORPORATED
245 Freight Street

54 Direct imaging process for forming resist pattern on a surface, and use thereof in fabricating printed circuit boards.

57 A process is described for the direct production of an imaged pattern of resist on a substrate surface (such as a pattern of etch-resistant organic resin material on the surface of a copper-clad dielectric in connection with a printed circuit board (PCB) fabrication process), which process utilizes thermo-resists rather than photoresists, i.e., compositions which undergo thermally-induced, rather than photo-induced, chemical transformations. A film of thermo-resist composition applied to the substrate surface is scanned by a focused heat source (e.g., a thermal laser emitting in the IR region) in a predetermined pattern, without a phototool, to bring about localized thermally-induced chemical transformations of the composition which either directly produce the resist pattern or produce in the film a developable latent image of the pattern.

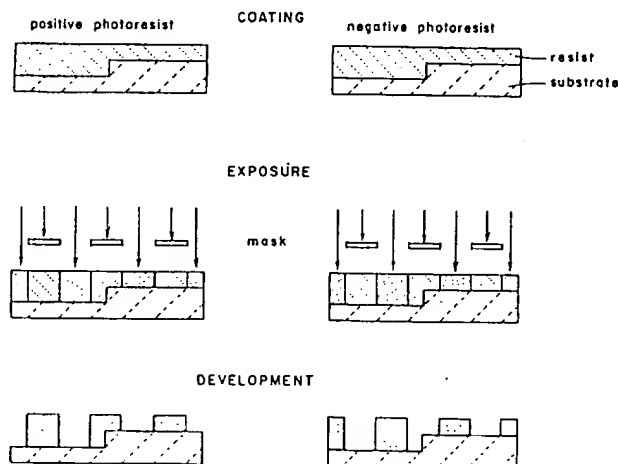


Fig. 1

EP 0 557 138 A2

BACKGROUND OF THE INVENTION

The present invention relates to the formation of a resist pattern on a substrate surface by a direct imaging process (i.e., without use of a phototool), and more particularly to the use of such direct imaging process in the fabrication of a printed circuit board.

A printed circuit board (PCB) fundamentally consists of a substrate made of dielectric material (such as epoxy, polyimide or the like, typically glass-reinforced) carrying a pattern of conductors on one or both of its faces. As used herein, PCBs are intended to include simple single- or double-sided PCBs; single- or double-sided innerlayer PCBs for use in fabricating multilayer PCBs; and multilayer PCBs per se.

Numerous techniques have been developed for forming the conductor pattern of PCBs, including subtractive techniques, additive techniques, and techniques involving both additive and subtractive aspects. Common to such methods is the reliance upon a patterned organic resist to define (either positively or negatively) selected surfaces of the board which will serve as the conductor pattern. Thus, for example, a dielectric substrate surface can be patterned with resist in the negative of the desired conductor pattern, followed by metal plating of the areas not covered by resist so as to provide the conductor pattern, followed by removal of the resist. In a more commonly employed method, the starting material is a dielectric having a metal layer (e.g., copper) covering one or both of its faces, and over which metal layer is arranged a resist pattern in the positive of the desired circuitry pattern. The metal areas not protected by resist are etched away down to the dielectric substrate surface, whereupon subsequent removal of the resist reveals the desired conductor pattern. In another common technique, the metal-clad dielectric is patterned with a first resist in the negative of the desired conductor pattern; the non-resist covered areas are then built up with further metal; the so-metallized patterned areas then protected by a second resist in the same pattern; the first resist then removed and the metal previously thereunder etched away; and the second resist then removed to reveal the desired conductor pattern.

Apart from resists utilized in the foregoing manners (in which uses they typically are referred to as "primary" resists), resists also are utilized to provide a permanent coating (known as a "solder mask") over selected surface areas of a PCB so as to protect these areas from corrosion, oxidation, etc., and to protect them during subsequent soldering steps carried out on the PCB. Use of resist in this manner often is referred to as a "secondary" resist.

The provision of necessary resist patterns in fabricating PCBs is at present effected almost exclusively with photoresists. Photoresists are applied to surfaces in question in the form of a film, but not directly in the ultimately desired resist pattern. Rather, the composition of the photoresist is such that it undergoes photo(light)-initiated change when exposed to a radiation source of appropriate wavelength (typically, UV radiation). Thus, by selective imagewise exposure of the photoresist film to radiation, there is created in the film a latent image which can then be developed to provide the desired resist pattern.

In particular, photoresists are formulated of photo-sensitive compositions such that the photo-initiated change which occurs upon exposure to activating radiation is to render the exposed areas differentially more or differentially less soluble in a developer than unexposed areas. The solubility difference thereby permits areas of the photoresist film to be selectively removed with developer while leaving behind other areas which serve as the resist pattern.

Photoresists may be either "positive"-working or "negative"-working. A positive photoresist is one in which the exposure to UV light irradiation brings about photo-initiated reactions which cause the so-exposed areas to become differentially more soluble in developer than the unexposed areas. These reactions may, e.g., be in the nature of a photo-induced depolymerization of polymeric resin materials in the composition through breaking of chemical bonds in the polymer chain; or photo-induced change in the structure of a compound present in the composition which enables the entirety of the composition, including its resin components, to become more soluble in developer; or other like reactions. A negative photoresist, on the other hand, is one in which the exposure to UV light irradiation brings about photo-initiated reactions which cause the so-exposed areas to become differentially less soluble in developer than unexposed areas, such as may occur through utilization of a composition which undergoes photo-initiated polymerization, additional polymerization or cross-linking, such as by free radical mechanisms. Accordingly, when using a positive photoresist, those portions exposed to UV light irradiation are selectively removed by developer, while in a negative photoresist, the developer selectively removes those portions which were not exposed to UV light irradiation (see Fig. 1).

For providing the necessary photoresist film used in producing primary resists, generally any of three types of photoresists can be employed. One type is known as a dry film, which is provided in the form of a pre-existing film which is then laminated to the substrate surface. See, e.g., U.S. Patent No. 3,469,982. Dry films, which in practice are exclusively negative photoresists, are overwhelmingly preferred today in mass

production of PCBs.

Another type of photoresist film is that obtained from a liquid photoresist composition (which may be a positive or negative photoresist) which is applied to the substrate as a film by roller coating, dipping, spinning or the like, followed by drying of the film to eliminate all or most of the solubilizing solvents used therein.

A third type of photoresist film is that obtained by electrophoretic deposition onto metal substrate surfaces, i.e., using a liquid photoresist composition which is formulated so as to be electrophoretically depositable. See, e.g., U.S. Patent Nos. 4,592,816; 4,751,172; and 5,004,672.

For the provision of solder masks, the photoresists employed are predominantly liquid, negative photoresist compositions applied as a film by roller coating, curtain coating or the like. A typical process for producing a solder mask can be found in U.S. Patent No. 4,789,620.

The imagewise exposure of the photoresist film, i.e., the exposure of only selected portions of it to UV light irradiation to produce the desired latent image, is predominantly effected through use of an appropriately patterned mask (phototool) which permits passage of UV light therethrough, to the film, only in the desired locations. The difficulty with such phototools is that their preparation is very expensive and time-consuming. Moreover, the use of phototools for selective imaging imposes limits on the achievable resolution of the conductor pattern for a variety of reasons.

In recent years, attention has been directed to so-called "direct imaging" techniques for photoresists. In these direct imaging methods, the exposure of only selected areas of the photoresist film to the activating radiation needed to bring about the required photo-initiated changes in the film composition does not utilize a radiation source directed through a patterned phototool, but rather employs a suitably focused beam of such radiation (such as with a laser of appropriate wavelength light) which directly scans the film in a predetermined (computer-controlled) desired tracking pattern. See, e.g., U.S. Patent No. 4,724,465; Kuchta, A.D., "Technological Requirements for Direct Imaging of Photoresists", Technical Paper No. A 8/1, Printed Circuit World Convention 5 (June 1990); Meier, K., "Laser Direct Imaging In High Definition Image Transfer Processes", Technical Paper No. A 8/2, Printed Circuit World Convention 5 (June 1990). While such techniques offer potential advantages in resolution capability and avoidance of defects sometimes caused by imperfect phototool artwork and/or by operator handling of phototools, those developed to date are too slow for mass production; require expensive photoresists; and rely upon lasers which have a short life unsuited for industrial use.

SUMMARY OF THE INVENTION

A primary object of the present invention is to provide a direct imaging process for forming a pattern of resist on a substrate surface.

A more particular object of the invention is to provide patterned resists in the course of fabricating a printed circuit, which patterned resists are provided by direct imaging of a suitably composed film in a desired predetermined pattern without use of a phototool.

Yet a further object of the invention is to provide a direct imaging process for selectively forming a desired imaged pattern in a film composition without reliance upon photosensitive materials or compositions.

These, and other objects as will be apparent, are accomplished by the provision of a process which makes use of compositions which, applied as a film to a substrate surface, can be selectively transformed through thermally-induced mechanisms which are mediated by an appropriately focused thermal energy beam which directly scans the film in a desired pattern and without use of a phototool. The so-produced selective transformations of the film composition either directly produce the desired resist pattern or produce a developable latent image thereof. In essence, the process of the invention relies upon the selective thermal inducing of compositional changes in a composition having thermally-sensitive properties as a means for producing a patterned resist from a generally unpatterned film composition, as opposed to processes which rely upon photosensitive properties of film compositions and selective light imaging thereof to produce the patterned resist.

Thermally-sensitive resist compositions for use in the invention, which are herein referred to as "thermo-resists", are of a type which undergo chemical transformation in response to exposure to, and absorption of, suitable heat energy. The nature of the thermally-induced chemical transformation may be to ablate the composition, or to increase the solubility of the composition in a particular developer, or to decrease the solubility of the composition in a particular developer. As such, selective heat exposure of predetermined areas of a film formed of the composition has the capability of directly or indirectly producing a suitably imaged pattern of composition which can serve, e.g., as a resist pattern in PCB

fabrication.

In a manner similar to that with photoresists, the thermo-resists of the invention can be positive-working or negative-working. With a positive thermo-resist, the selective exposure of the composition film to an appropriately focused beam of the requisite thermal energy will either (a) ablate the so-exposed composition, in which case there is directly produced the desired resist pattern represented by the remaining film portions not exposed to the focused heat energy and thus not ablated, or (b) cause the so-exposed composition to become differentially more soluble in a suitable solvent, in which case there is produced in the film what is essentially a latent image, such that contact of the film with a suitable developer will dissolve away the heat-exposed areas and leave behind the non-heat-exposed areas as the desired pattern. With a negative thermo-resist, selective exposure of the composition film to the appropriately focused beam of the requisite thermal energy causes the so-exposed areas to become differentially less soluble in a suitable developer, such that subsequent contact with the developer dissolves away the areas not heat-exposed and leaves behind the heat-exposed areas as the desired resist pattern.

Through use of thermo-resists, the ability to produce a resist pattern on a substrate surface by direct imaging without use of a phototool is greatly enhanced because the imaging beam need only be a suitably focused source of requisite thermal energy, such as can be formed from low-cost solid state lasers, as opposed to the focused source of radiation of particular wavelength required for direct imaging of photoresists. Focused thermal energy sources, such as an infrared (IR) laser beam, are inherently better suited for use in commercial-scale operations in terms of expense, life and reliability than the UV or deep UV beams needed for direct imaging of photoresists. Moreover, thermo-resist compositions, which need undergo only thermally-induced composition change rather than photo-induced change, are inherently less complicated than photoresist compositions in direct imaging processes. As such, not only can they be formulated in the cost-effective manner needed for industrial uses such as PCB fabrication, but their simpler mechanism of operation enables operation in daylight and the attainment of the processing speeds necessary for such uses and which heretofore have not been achievable using photoresist technology relying upon photo-initiated reactions.

In accordance, then, with the present invention, a direct imaging process is provided for the production of a resist pattern on a substrate surface, comprising the steps of:

- (a) applying to the surface a film of a thermo-resist composition, i.e., a composition which undergoes thermally-induced chemical transformation effective to ablate the composition or to increase or decrease its solubility in a particular developer; and then
- (b) in a predetermined pattern and without use of a phototool, directing to pre-selected areas of the film a suitably focused beam of thermal energy effective to there bring about the thermally-induced chemical transformation of the composition.

When the thermo-resist is one which undergoes thermally-induced ablation, the foregoing steps directly produce the desired resist pattern, as represented by the non-ablated film composition areas remaining on the surface. For the other types of thermo-resists, the steps produce essentially a latent image in the film; a subsequent step of contacting the film with the appropriate developer is then required in order to produce the desired resist pattern by dissolution from the surface of film areas which have been rendered differentially more soluble in the developer than other areas by reason of the thermally-induced composition changes.

The process has particular applicability to PCB fabrication processes, for use in providing a plating resist pattern, an etch resist pattern or a solder resist pattern. For example, the thermo-resist can be applied as a film to the metal surface (or surfaces) of a metal (e.g., copper)-clad dielectric substrate; followed by the selective directing to the film of a suitably focused thermal energy beam in the desired pattern, and without a phototool, such that there is directly, or after development in solvent, produced a resist pattern in the positive of the desired conductor pattern; followed then by etching away of the metal surface at those areas not covered by the resist. Removal (stripping) of the resist then reveals the desired conductor surface pattern for the PCB. In like manner, the process of the invention can be used in any PCB application for which photoresists have heretofore been employed.

According to more detailed aspects of the invention, the preferred means for focusing the requisite intensity of thermal energy to the film of thermo-resist composition so as to bring about the thermally-induced chemical transformation will be by way of an infrared (IR) beam, e.g., a laser beam emitted by a thermal laser such as a laser diode, Neodymium-Yag or CO₂ diode laser. Any other heat energy beam which can be focused to the extent required (as dictated by the degree of line definition involved with the particular pattern) can also be employed, such as a beam of solar light. The focused beam supplies a highly localized heat which induces the chemical transformation of the film and hence can be thought of as a "focused moving oven." The scanning of the film with the focused beam in the appropriate pattern can be

controlled, e.g., by a CAD device. See, e.g., Emmel, P.M., SPIE Proceedings 2, 222 (1980).

BRIEF DESCRIPTION OF THE DRAWINGS

5 FIG. 1 is a schematic representation of the formation of an imaged resist pattern on a substrate according to prior art methods employing photoresists. The substrate surface, e.g., the surface of an external metal coating of a dielectric board used for the manufacture of a PCB, is coated by a photoresist film, which may be a negative or a positive photoresist. A mask (phototool) is then put over the film and the entire surface is illuminated by UV light whereby part of the photoresist film is exposed to light. The light
10 exposure results in an increase in the solubility of the light exposed areas of the film relative to the unexposed areas in a suitable developer, (positive photoresist) or a decrease in the solubility of the light exposed areas relative to the unexposed areas in a suitable developer, (negative photoresist). Following development, i.e., contacting the film with an appropriate developer, the more soluble portions of the film are removed whereby the underlying substrate is revealed; in the case of the positive photoresist, the
15 revealed portions of the substrate correspond to the areas of the film which were exposed to light, while for a negative resist the revealed portions of the substrate correspond to the areas of the film not exposed to light.

FIG. 2 is a schematic representation of the formation of an imaged resist pattern on a substrate surface by the method of the invention utilizing a positive thermo-resist film. A substrate, which may be an external
20 copper layer of a dielectric board used for the manufacture of a PCB, is coated by a positive thermo-resist film. A focused beam of heat energy is then directed to preselected portions of the film by means of a computer-controlled scanning device, without use of a phototool, whereby the heat-activated portions of the film composition become more soluble in certain types of solutions than those film portions not heat-activated. Following development, i.e., contacting of the film with an appropriate developer, the portions of
25 the film which were selectively heat-activated are dissolved and the underlying substrate is there revealed.

FIG. 3 is a schematic representation of the formation of an imaged resist pattern on a substrate by the method of the invention utilizing a negative thermo-resist film. The method is in essence similar to that depicted in FIG. 2, the difference being in that the selective heat activation by means of the focused beam of heat energy causes a decrease in solubility of the heat-activated portions of the film relative to the
30 portions not heat-activated. Consequently, the portions of the substrate which are revealed after development are those underlying the portions of the film which were not heat-activated.

DETAILED DESCRIPTION OF THE INVENTION

35 In accordance with the present invention, an imaged pattern of material suitable as a resist is provided on a surface by first providing a film of a thermo-resist composition on the surface, and then, in a predetermined pattern and without use of a phototool, directing to particular areas of the film an appropriately focused beam of thermal energy effective to bring about at such areas a thermally-induced chemical transformation of the composition, with result of either directly producing the desired imaged resist
40 pattern or producing a developable latent image of such pattern.

In the most preferred embodiment of the invention, the appropriately focused beam of thermal energy will take the form of an IR beam produced by a thermal laser. In describing the invention hereinafter, and particular aspects of thermo-resist compositions and the like, use of the foregoing focused thermal energy will be assumed in illustration of the invention and for ease of description.

45 The thermo-resist compositions suitable for use in the invention are compositions which comprise polymeric components, or precursors thereof, selected so that the imaged pattern eventually produced therefrom will itself constitute a composition which possesses the physical and chemical properties suitable for its intended purpose (e.g., resistance to etchant solutions when used as an etch resist for a PCB; resistance to solder when used as a solder mask for a PCB; etc.). In addition, the thermo-resist
50 compositions are formulated such that they possess the property of undergoing thermally-induced chemical transformation effective either to ablate the composition or to increase or decrease its solubility in a particular developer.

These thermo-resist compositions typically will be employed in liquid form in association with a suitable organic solvent, and will be applied to the surface in question as a film, having a thickness of e.g., from
55 about 10 - 100 μm , by any suitable method. After application, the thermo-resist film will be dried under conditions suitable to evaporate all or most of the solvent (and avoiding, of course, any conditions which might prematurely bring about the thermally-induced chemical transformations later involved in the direct imaging process). As with photoresists, the thermo-resists also can be formulated so as to be elec-

trophoretically depositable onto conductive surfaces, such as the copper-clad surface of a printed circuit board material.

The thermo-resist compositions also can be provided in the form of a dry film, in which case the film will be applied to the surface in question by suitable lamination technique. As described in the earlier-noted U.S. Patent No. 3,469,982, and as is well understood in the art, dry film photoresists comprise a substantially solid thin layer of photoresist composition wherein at least one, and preferably both, surfaces of the layer are in removably adherent contact with a thin flexible polymeric film, such as a polyester, a polyolefin, a polyamide, a vinyl polymer, a cellulose ester, and the like. The dry films are prepared by coating a liquid photoresist composition onto a suitable polymeric film (typically referred to as a backing or support sheet), and then drying the composition to obtain a substantially solid layer thereof removably adhered to the backing sheet. In the case where the dry film is one in which both surfaces of the photoresist layer are in contact with a polymeric film (i.e., sandwiched between two polymeric films), a second polymeric film (typically referred to as a protective or cover sheet) will be arranged on the photoresist layer surface opposite the surface which is in contact with the backing sheet. For use of the dry film to produce a resist pattern, the dry film (with the protective sheet, if originally present, removed) is laminated to the substrate surface in question, using suitable heat and pressure, so that a surface of the photoresist layer is in direct contact with the substrate surface. At this point, the now outer-facing backing sheet can be removed for imagewise exposure of the photoresist layer to activating radiation. More typically, the backing sheet is a polymeric film which is transparent to the radiation (e.g., polyethylene terephthalate (MYLAR[®])), such that the light exposure can be effected without removal of the backing sheet.

For the thermo-resist compositions of the present invention, the preparation and use of dry film forms thereof is essentially the same as known for photoresist compositions. Liquid thermo-resist composition is coated to a suitable layer thickness onto a flexible polymeric film and then dried to obtain a substantially solid layer of thermo-resist composition removably adhered to the polymer film. As with photoresists, it is also possible, and preferred, to have a polymeric film in removably adherent contact with the opposite surface of the thermo-resist layer, i.e., so that the dry film thermo-resist comprises a sandwich structure of polymer film, thermo-resist, and polymer film. Heat and pressure lamination techniques are then used to apply the thermo-resist layer to the substrate surface in question; where the dry film is of the aforementioned sandwich structure, then, one of the polymeric film sheets will be preliminarily removed so that a surface of the thermo-resist layer is adhered directly to the substrate surface. Since the pattern imaging of the thermo-resist relies upon heat rather than radiation, the outer-facing polymeric film sheet typically and preferably will be removed before thermal imaging occurs, although this is not strictly required. Also, as discussed later herein, certain embodiments of this invention involve use of a photo-exposure step prior to thermal imaging, and in those embodiments the outer-facing polymeric film, if arranged to be transparent to the activating radiation, can be left in place until after the photo-exposure step.

One class of thermo-resist compositions for use in the invention, and which operate as positive-working thermo-resists, are compositions which are formulated so as to ablate as a result of exposure to the thermal energy (e.g., exposure to a high intensity thermal beam, suitably one emitted by a high intensity thermal laser). Thermo-resists of this type preferably comprise suitable organic resist substances in which have been suspended metal-based, carbon or other finely-divided particles. These particles aid in the absorption of the directed thermal energy, resulting in evaporation or volatilization of the film composition. See N. P. Frnzikov et al, Khim.Fiz. 9, 1354 (1990). Thus, when a film of such thermo-resist composition is applied over a surface and a focused beam of thermal energy then used to scan the film according to a desired pattern, and without use of a phototool, those film areas exposed to the beam will ablate and directly reveal the underlying surface. Those film areas not exposed to the beam will thus remain on the substrate surface to serve as the appropriate pattern of resin for the desired purpose (e.g., etch resist in PCB fabrication).

The other class of thermo-resists for use in the invention, and which can be formulated so as to be positive- or negative-working, are compositions which undergo a thermally-induced chemical transformation effective to make them more soluble or less soluble in a particular developer. With films formed from these thermo-resists, the scanning of the film with the thermal energy beam in a particular pattern, without use of a phototool, brings about highly localized solubility-increasing or solubility-decreasing compositional changes confined to the areas exposed to the beam, with result that the film carries a latent image of the exposure pattern. Subsequent contact with an appropriate developer then produces the desired pattern of composition.

Positive thermo-resists of this type can be those in which bonds in the polymeric and/or non-polymeric molecules of the composition are broken as a result of heat exposure. As such, selective heat exposure causes the so-exposed areas to become differentially more soluble in developer than the intact composition areas not so exposed to the heat energy. Examples of such positive thermo-resists which can be used in

the process of the invention are those comprising phenolic polymers and/or monomers, in which free hydroxyl groups are protected, and an acid or a substance which may release an acid upon heating. The change in the solubility of these organic compositions following heating is a result of the tendency of certain protecting groups to leave the molecule upon heating in the presence of acid catalysis, e.g., acid cleavage

5 of ethers, hydrolysis of esters in the presence of an acid, or the like.

Particular examples of such polymers which can be included in positive thermo-resists are phenolic polymers of the novolac family (products of the condensation of phenol or cresol with formaldehyde in an acid catalysis) such as epoxy-novolac (reaction products between novolacs and epichlorohydrin), or poly (vinylphenols) (obtained by cationic or radical polymerization). The hydroxyl protecting groups may be

10 ethers, such as alkyl-, benzyl-, cycloalkyl- or trialkylsilyl-ethers, and oxy-carbonyl groups.

Negative thermo-resists can be based upon a thermally-induced polymeric cross-linking reaction. As such, selective heat exposure causes the so-exposed areas to become differentially less soluble in developer than the intact composition areas not so exposed to the activating heat energy.

Negative thermo-resists which can be used in the process of the invention may be of two general types.

15 Resists of the first type comprise a polymer such as epoxy resin or epoxy-novolac resin, aliphatic-aromatic-, or heteroaromatic-polyamine resin as a cross-linking agent and an acid or a compound which releases an acid upon heating. Examples of the cross-linking agent that may be used according to the present invention include diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, diethylene propylamine, o-, m- and p-phenylene diamine, bis (4-aminophenyl methane), bis(4aminophenyl) ether, 2-

20 methyl-imidazole, 2-ethyl-4-methyl imidazole and 1-benzyl-2-methyl imidazole.

The second type of negative thermo-resists that may be used in accordance with the present invention comprise a novolac polymer, a photoinitiator which generates acid upon exposure to actinic radiation and a cross-linking agent capable of reacting with novolac polymers when heated in the presence of an acid. Examples of such photoinitiators are esters or amides of 2-diazo-1,2-naphthoquinone-4-sulfonic acid, o-

25 nitrobenzaldehydes and esters derived from nitrobenzyl alcohol, α -haloacylphenons, onium salts such as chlorides, bromides and iodides of onium bases of elements in group VA, VIA or VIIA of the Periodic Table and methane-sulfonate esters of aromatic compounds. Examples of cross-linking agents which may be used in this type of negative thermo-resist composition are hexamethylmelamine alkylethers, resols (products of the condensation of phenol or cresols with formaldehyde in a base catalysis), 2,6-bis-(hydroxymethyl)-4-

30 methyl phenol and epoxy resins. When a composition of this type is used, the process also includes the initial step of a non-selective flood exposure of the film to actinic radiation (without the use of phototools). This flood exposure causes the included photoinitiator to generate the acid (and acid environment) necessary to allow the subsequent thermally-induced chemical transformation of the film composition upon exposure to appropriate heat energy, i.e., to catalyze the thermally-induced cross-linking reactions. The creation of the acid environment also serves to render those composition film portions not heat exposed

35 acidic enough for aqueous-base development.

For those thermo-resists of the foregoing types, i.e., those not based upon ablation, the selective heat exposure is, of course, then followed by contact of the film with an appropriate developer which removes from the substrate surface the composition film portions which have been rendered differentially more

40 soluble in such developer by reason of the heat imaging (i.e., the heat-exposed areas for a positive-working thermo-resist or the non-heat-exposed areas for a negative-working thermo-resist). Any number of suitable types of developer can be employed, such as organic solvents, oil-in-water or water-in-oil emulsions, in particular micro-emulsions, basic aqueous solutions of alkali metal salts (e.g., hydroxides, carbonates) and the like.

45 It will be appreciated that the surface to which the thermo-resist composition is applied as a film preferably will be pretreated in appropriate manner in order to obtain optimal adhesion of the composition thereto. Where the substrate surface is highly reflective, measures also should be taken to avoid adverse effects which may be caused by reflection of the thermal energy beam. To reduce reflectivity and maximize the thermal absorption of the film composition, one may resort to use of appropriate fillers in the

50 composition to decrease its transparency.

As previously noted, the preferred focused source of heat energy will be a thermal laser capable of producing thermal energy, such as a laser diode, carbon dioxide laser, or Neodymium-Yag laser. The output of the CO₂ laser lies in the infrared and the highest gain transition is at 10.6 μ m. The Neodymium-Yag lasers are capable of operation at high average power levels, at the wavelength of 1.06 μ m. Laser diodes

55 typically operate near 0.8 μ m. Although the foregoing thermal energy sources are preferred, any other appropriate means of providing for any given composition the requisite thermal energy in a focused manner sufficient for the degree of line definition required for any particular purpose can be employed. For industrial-scale production of, e.g., PCBs, where speed of processing can be of decided importance, it

generally will be the case that the choice of thermal energy source will be one having the highest possible intensity such that the required thermally-induced chemical transformations of the thermo-resist composition film occur in very rapid manner.

By reason of the present invention there is provided a direct imaging process, i.e., one without the use of phototools, which possesses all the inherent advantages of direct imaging but which is not plagued by the associated problems heretofore exhibited by direct image processes which rely solely upon photoresist compositions and expensive lasers. Thus, the process avoids the time and expense of phototool preparation and the defects which may occur in the artwork per se or as a consequence of operator handling of the phototool. In contrast to photoresist-based direct imaging processes, however, the present process, through reliance upon thermally-induced reactions rather than solely light-induced reactions, readily enables the use of inexpensive compositions and avoids the short life and slow speeds associated with the UV or Deep UV lasers required when using photoresist compositions. For PCB fabrication in particular, the present invention enables realization of the current industry direct imaging goal of scanning in 20-30 seconds or less an 18"/24" coated panel with cost-effective lasers.

In addition, by providing a process based upon thermolysis (i.e., in which chemical changes are due to heat) rather than photolysis (i.e., in which chemical changes are due solely to light), the invention enables utilization of varieties of thermo-resist compositions whose chemistry may be tailored to obtain optimal results. The thermo-resist composition may be based on simple non-expensive polymers such as epoxy polymer which is the preferred constituent of the dielectric substrates and of solder masks of PCBs.

Finally, the process of the present invention allows the use of essentially aqueous developing solutions, which in itself is a highly desirable object for protecting the environment.

The process of the present invention is further illustrated hereinafter with reference to some non-limiting specific Examples.

EXAMPLE 1

A positive thermo-resist composition was prepared from the following constituents:

	% (w/w)
poly(vinylphenol) - 100% substituted by t-butyloxycarbonyl	80
p-toluenesulfonic acid	5
ethylmethyl ketone (solvent)	15

The p-toluenesulfonic acid was added just prior to use of the composition.

The composition was spin-coated onto a surface of a copper substrate to achieve a layer of about 15 μm thickness. Spin-coating was done at 2000 rpm for 20 seconds. The film was then dried by an air current and scanned, in a predetermined pattern dictated by a CAD device, by an IR beam from a Neodymium-Yag laser emitting light at 1.06 μm . Following scanning, the film was developed by immersing the board in an aqueous solution of 1% NaOH for 60 seconds, resulting in removal from the copper substrate of those film composition areas heat-activated by the IR beam, and achievement of a well defined resist pattern made up of the film composition areas remaining on the substrate.

EXAMPLE 2

A negative thermo-resist composition was prepared from the following constituents:

	% (w/w)
Epoxy resin DEN 438™	32
sorbic acid	8
cyclohexanone (solvent)	59
phenylene diamine (cross-linking agent)	1

The phenylene diamine was added just prior to use of the composition.

The composition was applied onto the copper surface of a board and a uniform film of about 45 μm thickness was obtained by spinning. The film was then dried using an air current, scanned by an IR laser as

in Example 1 and then developed by immersion in cyclohexanone for 60 seconds to effect removal from the substrate of the film composition areas not heat activated by the IR beam. A clearly defined resist pattern was obtained from the heat activated film composition areas remaining on the substrate.

5 EXAMPLE 3

A negative thermo-resist composition was prepared from the following ingredients:

10		% (w/w)
	Quatrex 2410	9.5
	poly(vinylphenol)	28.3
	sorbic acid	4.7
	phenylene diamine	0.8
15	cyclohexanone	56.7

The phenylene diamine was added just prior to use of the composition.

20 The process of Example 2 was repeated except for the development which in this case was performed by immersion in a micro emulsion of:

	% (w/w)
cyclohexanone	18.4
Pluronic L-64	1.2
oleic acid	0.4
25 water	80.0

for 2.5 minutes at 35 °C. A satisfactory pattern was achieved.

30 EXAMPLE 4

The procedure of Example 3 was repeated but with a negative thermo-resist in which methacrylic acid was used in place of the sorbic acid.

35 The developer used in this example was an aqueous solution of 2% NaOH (90 seconds at 40 °C). A well defined pattern was obtained.

EXAMPLE 5

40 A negative thermo-resist composition was prepared by mixing the following constituents:

	% (w/w)
45 Novolac Resin	6
ester of 2-diazo-1,2-naphthoquinone -4-sulfonic acid with trihydroxybenzophenone (photosensitizer)	4
poly(vinylphenol)	30
2,6-bis(hydroxymethyl)-4-methylphenol (cross-linking agent)	3
50 solvent*	57

*a 3:2 mixture of propylene glycol mono-methyl ether acetate and n-butanol

A copper board was coated by spinning with the above composition to obtain a uniform layer of about 20 µm thickness in a similar manner to that described in Example 1. The film was then dried in an oven at 90 °C for 30 minutes and flood exposed to a broad band UV radiation for 2 minutes. The film was then scanned by a thermal (IR) laser (the same laser as in Example 1) beam and developed by an aqueous solution of 1% KOH for 75 sec. A satisfactory pattern was achieved.

EXAMPLE 6

A positive thermo-resist was prepared by admixing:

	% (w/w)
Maruzen 5000 t-BOC	46.6
Benzoyl peroxide	6.7
Diphenyl iodonium hexafluorophosphate	6.7
Methyl ethyl ketone	40.0

Maruzen 5000 is poly(vinylphenol) having a molecular weight of about 5000, and was 100% substituted with t-butyloxycarbonyl.

This composition was spin-coated onto a copper substrate surface to a thickness of 20 μm and then dried by an air current. A UV laser was used to scan the film in a predetermined (CAD-directed) pattern (a deep UV laser also would be suitable), with result of causing the onium salt to generate acid at the film composition areas exposed to the UV radiation. Thereafter, the thermal laser of Example 1 scanned the film in the same pattern used for the UV laser, with result that the heat-activated areas underwent acid-catalyzed breaking of bonds of the t-BOC. The heat-activated areas were then removed from the substrate using an aqueous solution of 1% NaOH (60 seconds).

It should be appreciated that the foregoing process can be modified by elimination of the UV laser, and reliance solely upon the thermal laser to generate acid from the onium salt (in the presence of benzoyl peroxide or any other oxidizing or reducing agent) as well as then to bring about the acid-catalyzed bond breaking of the t-BOC.

EXAMPLE 7

A negative thermo-resist suitable for use as a solder mask was prepared by first admixing the following components in the indicated weight percentages:

	% (w/w)
Butyl carbitol	33.0
Cellosolve acetate	1.6
Epoxy resin	50.0
Flow additive	1.6
Colorant	4.5
Silica	5.0
Water	4.3

Prior to use, this first composition was admixed with methyl dianiline (8% w/w). The resultant liquid composition was curtain coated onto a patterned printed circuit to a film thickness of about 20 μm , and then dried by an air current. The film was then scanned in a CAD-directed pattern using the thermal laser of Example 1, such that all surface areas of the film-coated printed circuit other than areas constituting through-hole surfaces, surrounding pads and lands were exposed to the laser. By development with butyl carbitol, the film areas which were not exposed to the laser were removed, with result that the composition film areas remaining formed the desired solder resist pattern.

EXAMPLE 8

A thermo-resist composition was prepared by admixing the following components in the indicated weight percentages:

	% (w/w)
Maruzen 5000 - t-BOC (100%)	20.0
Diphenyl Iodonium Hexafluoro Phosphate	5.0
Quatrex 2410	33.0
Cyclohexanone	29.0
Methyl ethyl ketone	13.0

5 This liquid composition was spin coated onto a copper-clad PCB material to a film thickness of about 20 μm , and then dried in an air current. The film was then scanned in a CAD-directed pattern using the thermal laser of Example 1, with result that the film areas exposed to the laser were completely ablated from the copper surface. The film areas not exposed to the laser remained on the copper surface in a clearly defined resist in the desired pattern.

15 Although the invention has been described in detail with reference to particular preferred embodiments and examples, it will be understood that such description is presented in illustration rather than limitation of the invention, the scope of which is defined in the appended claims.

Claims

- 20 1. A direct process for producing an imaged resist pattern on a substrate surface, comprising the steps of:
 - (a) applying to said surface a film of a thermo-resist composition, which composition has the property of undergoing a thermally-induced transformation effective either to ablate the composition or to increase or decrease its solubility in a particular developer;
 - 25 (b) thereafter, in a predetermined pattern and without use of a phototool, directing to selected areas of said film, corresponding to the positive or negative of the desired resist pattern, a focused beam of heat energy effective to there bring about in said composition the said thermally-induced transformation; and
 - (c) where the thermally-induced transformation is other than ablation, thereafter contacting said film with a developer effective to selectively remove from said substrate surface those areas of said composition which, by reason of said transformation, are differentially more soluble in said developer.
- 30 2. A direct process for producing an imaged resist pattern on a substrate surface, comprising the steps of:
 - 35 (a) applying to said surface a film of a thermo-resist composition, which composition has the property of undergoing a thermally-induced chemical transformation effective to increase or decrease its solubility in a particular developer;
 - (b) thereafter, in a predetermined pattern and without use of a phototool, directing to selected areas of said film, corresponding to the positive or negative of the desired resist pattern, a focused beam of heat energy effective to there bring about in said composition the said thermally-induced chemical transformation; and
 - 40 (c) thereafter contacting said film with a developer effective to remove from said substrate surface those areas of said composition which, by reason of said transformation, are differentially more soluble in said developer.
- 45 3. A direct process for producing an imaged resist pattern on a substrate surface, comprising the steps of:
 - (a) applying to said surface a film of a thermo-resist composition, which composition has the property of undergoing a thermally-induced chemical transformation effective to increase its solubility in a particular developer;
 - 50 (b) thereafter, in a predetermined pattern and without use of a phototool, directing to selected areas of said film, corresponding to the negative of the desired resist pattern, a focused beam of heat energy effective to thermally induce the chemical transformation which increases the solubility of said selected areas of said film in said particular solvent; and
 - (c) thereafter contacting said film with said developer so as to remove said selected film areas from said surface and thereby producing a resist pattern constituting the areas of said film other than said selected areas.
- 55 4. A direct process for producing an imaged resist pattern on a substrate surface, comprising the steps of:

(a) applying to said surface a film of a thermo-resist composition, which composition has the property of undergoing a thermally-induced chemical transformation effective to decrease its solubility in a particular developer;

5 (b) thereafter, in a predetermined pattern and without use of a phototool, directing to selected areas of said film, corresponding to the positive of the desired resist pattern, a focused beam of heat energy effective to thermally induce the chemical transformation which decreases the solubility of said selected areas of said film in said particular solvent; and

10 (c) thereafter contacting said film with said developer so as to remove from said surface the film areas other than said selected areas of said film, thereby producing a resist pattern constituting said selected areas of said film.

5. A process according to Claim 3 wherein said thermo-resist composition comprises (a) a first member selected from the group consisting of a phenolic polymer, a phenolic monomer and combinations thereof, in which the free hydroxyl groups thereof are protected, and (b) a second member selected from the group consisting of an acid, a substance which releases an acid upon heating and combinations thereof.

6. A process according to Claim 5 wherein said phenolic polymer is selected from the group consisting of a novolac, an epoxy-novolac, a poly(vinylphenol) and combinations thereof.

7. A process according to Claim 6 wherein said free hydroxyl groups of said phenolic polymer are protected by a chemical group selected from ether, oxy-carbonyl and combinations thereof.

8. A process according to Claim 4 wherein said thermally-induced chemical transformation of said thermo-resist composition effective to decrease its solubility in said particular developer comprises polymeric cross-linking.

9. A process according to Claim 8 wherein said thermo-resist composition comprises a cross-linkable polymer, a cross-linking agent for said polymer, and a member selected from the group consisting of an acid, a substance which releases an acid upon heating and combinations thereof.

10. A process according to Claim 9 wherein said cross-linkable polymer is selected from the group consisting of epoxy resin, epoxy-novolac resin and combinations thereof, and wherein said cross-linking agent is selected from the group consisting of aliphatic polyamine, aromatic polyamine, heteroaromatic polyamine and combinations thereof.

11. A process according to Claim 10 wherein said cross-linking agent is selected from the group consisting of diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, diethylene propylamine, o-phenylene diamine, m-phenylene diamine, p-phenylene diamine, bis(4-aminophenyl) methane, bis(4-aminophenyl) ether, 2-methylimidazole, 2-ethyl-4-methyl imidazole, 1-benzyl-2-methyl imidazole, and combinations thereof.

12. A process according to Claim 8 wherein said thermo-resist composition comprises a novolac polymer, a photoinitiator which releases an acid upon UV irradiation, and a cross-linking agent which reacts with said novolac polymer when heated in the presence of acid, and wherein said process comprises the further step, after step (a) and prior to step (b), of exposing said film composition to UV radiation effective to release said acid in said composition.

13. A process according to Claim 12 wherein said cross-linking agent is selected from the group consisting of hexamethylmelamine alkylether, resol, 2,6-bis-hydroxymethyl)-4-methyl phenol, epoxy resin, and combinations thereof.

14. A process according to Claim 12 wherein said photoinitiator is selected from the group consisting of esters or amides of 2-diazo-1,2-naphthoquinone-4-sulfonic acid, o-nitrobenzaldehydes and esters derived from nitrobenzyl alcohol, α -haloacylphenons, onium salts, methanesulfonate esters of aromatic compounds and combinations thereof.